

# Phase Relations in the Systems $\text{TiO}_2\text{--IrO}_2$ and $\text{SnO}_2\text{--IrO}_2$ in Air

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The pseudobinary systems  $\text{TiO}_2\text{--IrO}_2$  and  $\text{SnO}_2\text{--IrO}_2$  were studied by x-ray diffraction after treatment at various temperatures in air. Their equilibrium phase diagrams were similar, with no intermediate phases detected in either system. Maximum solid solution of  $\text{TiO}_2$  occurs with the addition of about 5 mole percent  $\text{IrO}_2$  at 1040 °C. Solid solution of  $\text{TiO}_2$  in  $\text{IrO}_2$  extends to a maximum of about 12 mole percent  $\text{TiO}_2$  at 1040 °C, the dissociation temperature. Limited solid solubility of  $\text{SnO}_2$  in  $\text{IrO}_2$  exists up to 3 mole percent  $\text{SnO}_2$  at the dissociation temperature, 1025 °C. Solid solution in  $\text{SnO}_2$  was not detected at temperatures up to 1400 °C.

Key Words: Dissociation, phase relations,  $\text{SnO}_2\text{--IrO}_2$  system, solid solution,  $\text{TiO}_2\text{--IrO}_2$  system

## 1. Introduction

The National Bureau of Standards has initiated a program to obtain accurate melting points of some of the metal oxides [1].<sup>1</sup> As part of this program, it is important to determine the suitability of various refractory metals as container materials. The effects various container materials have upon the oxides can be best established through a study of their equilibrium phase relations. The present work presents the results of an investigation of the phase relations between  $\text{IrO}_2$  and  $\text{TiO}_2$  and between  $\text{IrO}_2$  and  $\text{SnO}_2$ .

Powdered Ir has a strong tendency to oxidize to  $\text{IrO}_2$  when heated in air at moderate temperatures. However, complete oxidation is difficult to achieve. By utilizing  $\text{IrO}_2$  rather than Ir metal, the approach to equilibrium could be achieved more readily. The study would still reflect, however, the behavior in air of Ir metal in combination with  $\text{TiO}_2$  or  $\text{SnO}_2$ .

Iridium has a face-centered cubic, copper-type structure with  $a=3.8394$  Å [2]. The freezing point of Ir, 2443 °C, is given as a secondary reference point on the International Practical Temperature Scale (IPTS)<sup>2</sup> [3]. Iridium dioxide is similar to  $\text{TiO}_2$  in having the tetragonal, rutile structure with  $a=4.4983$  Å and  $c=3.1544$  Å [4].

Titanium dioxide occurs in two tetragonal polymorphic forms: anatase; and rutile ( $a=4.594$  Å,  $c=2.958$  Å) [5], the stable modification. The unit cell dimensions of  $\text{SnO}_2$  (tetragonal) have been reported as  $a=4.738$  Å,  $c=3.188$  Å [6]. Several melting points of  $\text{TiO}_2$  have been reported, the values ranging from 1820 to 1850 °C in an air environment [1]. Two melting

points have been reported for  $\text{SnO}_2$ , 1630 and 1637 °C [1].

## 2. Materials

The starting materials used in this study were found by general quantitative spectrochemical analyses<sup>3</sup> to have the following impurities:

- $\text{IrO}_2$ : 0.01–0.1%, Pt;  
0.001–0.01% each Al, Cu, Fe, Pd, and Si;  
0.0001–0.001% Mg; and < 0.0001% Ca
- $\text{TiO}_2$ : 0.01–0.1% Si;  
0.001–0.01% Mg;  
0.0001–0.001% Cu; and < 0.0001% Ca
- $\text{SnO}_2$ : 0.01–0.1% each Bi, Co, and Fe;  
0.001–0.01% each Al, Cu, Ni, Pb, and Si;  
< 0.001% each Ag, Ca, In, Mg, and Mn.

## 3. Experimental Procedure

Specimens for the studies were prepared from 0.4 g batches of various combinations of the end members. Calculated amounts of each oxide, corrected for ignition loss, were weighed to the nearest milligram. Each batch was thoroughly hand mixed, placed in Vycor tubes (sealed at one end) and fired in a muffle furnace for a minimum of 18 hr at each of the following temperatures, 800, 900, and 1000 °C. Succeeding each heat treatment, the materials were thoroughly hand mixed and examined by x-ray diffraction techniques.

Following the preliminary heat treatments, portions of each batch were placed in small Vycor tubes and

<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

<sup>2</sup> This scale (IPTS) applies to all temperatures listed in this paper.

<sup>3</sup> The spectrochemical analyses were performed by the Spectrochemical Analysis Section of the National Bureau of Standards.

fired in a platinum alloy wire-wound quench furnace at various temperatures for different periods. The Vycor tube containing the specimen was air quenched by quickly pulling the tube from the furnace. Equilibrium was assumed to have been achieved when the x-ray pattern showed no change after successive heat treatments or when the data were consistent with the results from a previous set of experiments.

As  $\text{IrO}_2$  is heated near its dissociation temperature, it becomes somewhat volatile. The problem of volatility of  $\text{IrO}_2$  was minimized greatly by reacting the end members at low temperatures. In an attempt to maintain composition and obtain maximum reaction, sealed platinum tubes were employed as specimen containers for the prolonged heat treatments at temperatures below dissociation. The use of Vycor tubes instead of platinum for experiments at the higher temperatures was necessary because Ir, frequently found as a decomposition product, readily reacts with platinum. On the other hand, the Vycor tube did not appear to influence or react with the various oxide samples.

Temperatures in the quench furnace were measured with a 100 percent Pt versus 90 percent Pt-10 percent Rh thermocouple. All reported temperatures pertaining to quench furnace data are considered accurate to within  $\pm 5^\circ\text{C}$ . The precision of the measurements was  $\pm 2^\circ\text{C}$ .

An induction furnace utilizing an iridium crucible as both the susceptor and specimen container was used for the heat treatments above  $1400^\circ\text{C}$ . Temperatures were measured with a calibrated optical pyrometer sighted through a small hole in the crucible cover. The optical pyrometer temperature measurements are estimated to be accurate to within  $\pm 25^\circ\text{C}$  or better.

All specimens were examined by x-ray diffraction at room temperature using a high angle recording Geiger counter diffractometer and Ni-filtered Cu radiation.

## 4. Results and Discussion

### 4.1. $\text{TiO}_2\text{-IrO}_2$ and $\text{SnO}_2\text{-IrO}_2$ Systems in Air

The equilibrium phase diagram for the  $\text{TiO}_2\text{-IrO}_2$  system in air is given in figure 1. The diagram was constructed from the data listed in table 1. The circles indicate the compositions and temperatures of the experiments. It should be emphasized that figure 1 represents a composite of the systems  $\text{TiO}_2\text{-Ir}$  and  $\text{TiO}_2\text{-IrO}_2$  in the Ti-Ir-Oxygen ternary system. At the lower temperatures, the oxygen content of the specimens closely conforms to the compositions represented by the pseudobinary  $\text{TiO}_2\text{-IrO}_2$  system. At the higher temperatures; the compositions of the solid phases change by an apparent oxygen loss to those generally indicated by the  $\text{TiO}_2\text{-Ir}$  join. Considering this dissociation as a type of phase transition in which the vapor phase is ignored, figure 1 is a binary representation of a portion of the ternary system.

It was found in earlier work that  $\text{IrO}_2$  dissociates to Ir metal and presumably oxygen at  $1020^\circ\text{C} \pm 5^\circ\text{C}$  in

TABLE 1. Experimental data for compositions in the  $\text{TiO}_2\text{-IrO}_2$  system

Composition		Heat Treatment <sup>a</sup>		X-ray diffraction analyses <sup>b</sup>	Remarks
$\text{TiO}_2$	$\text{IrO}_2$	Temp.	Time		
Mole %	Mole %	$^\circ\text{C}$	hr		
98	2	900	45	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}}$	Very small amount of $\text{IrO}_{2\text{ss}}$ .
		<sup>c</sup> 1000	18	$\text{TiO}_{2\text{ss}}$	
		1050	2	$\text{TiO}_{2\text{ss}}$	
		1075	3	$\text{TiO}_{2\text{ss}}$	
		1125	3	$\text{TiO}_{2\text{ss}}$	
		1200	4	$\text{TiO}_{2\text{ss}}$	
		1300	3	$\text{TiO}_{2\text{ss}}$	
		1400	2	$\text{TiO}_{2\text{ss}} + \text{Ir}$	
		900	48	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}}$	
		<sup>c</sup> 1000	60	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}}$	
95	5	<sup>c</sup> 1000	336	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}}$	Quenched in ice water. Furnace cooled.
		1035	2	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}}$	
		1040	2	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}} + \text{Ir}$	Nonequilibrium. Nonequilibrium.
		1045	2	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}} + \text{Ir}$	
		900	48	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}}$	
90	10	<sup>c</sup> 1000	60	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}}$	Quenched in ice water. Furnace cooled.
		<sup>c</sup> 1000	336	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}}$	
		1035	2	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}}$	Nonequilibrium.
		1040	2	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}} + \text{Ir}$	
		900	18	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}}$	
75	25	<sup>c</sup> 1000	60	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}}$	Nonequilibrium. Nonequilibrium.
		<sup>c</sup> 1030	504	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}}$	
		1035	2	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}}$	Nonequilibrium. Nonequilibrium.
		1040	2	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}} + \text{Ir}$	
		1300	0.5	$\text{TiO}_{2\text{ss}} + \text{Ir} + \text{IrO}_{2\text{ss}}$	
50	50	<sup>d</sup> 1700	3	$\text{TiO}_2 + \text{Ir}$	High temperature x-ray data.
		500	0.5	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}}$	
		900	20	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}}$	
		975	0.5	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}}$	High temperature x-ray data. High temperature x-ray data. High temperature x-ray data.
		1000	0.5	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}}$	
		1000	3	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}}$	
		1000	18	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}}$	Quenched in ice water. Furnace cooled.
		<sup>c</sup> 1000	18	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}}$	
		<sup>c</sup> 1000	60	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}}$	
		1003	64	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}}$	Nonequilibrium. Nonequilibrium. Nonequilibrium.
		1020	66	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}}$	
		1025	66	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}}$	
		1030	3	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}}$	Nonequilibrium. Nonequilibrium. Nonequilibrium.
		1030	504	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}}$	
		1035	2	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}}$	
25	75	1040	2	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}} + \text{Ir}$	Nonequilibrium. Nonequilibrium. Nonequilibrium.
		1045	2	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}} + \text{Ir}$	
		1050	2	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}} + \text{Ir}$	
		1055	2	$\text{TiO}_{2\text{ss}} + \text{IrO}_{2\text{ss}} + \text{Ir}$	Nonequilibrium. Nonequilibrium. Nonequilibrium.
		1100	1.5	$\text{TiO}_{2\text{ss}} + \text{Ir} + \text{IrO}_{2\text{ss}}$	
		1100	40	$\text{TiO}_{2\text{ss}} + \text{Ir} + \text{IrO}_{2\text{ss}}$	
		1200	3	$\text{TiO}_{2\text{ss}} + \text{Ir}$	Nonequilibrium; $\text{IrO}_2$ probably formed on cooling.
		1300	0.5	$\text{TiO}_{2\text{ss}} + \text{Ir}$	
		<sup>d</sup> 1700	3	$\text{Ir} + \text{TiO}_2 + \text{IrO}_2$	
		900	18	$\text{IrO}_{2\text{ss}} + \text{TiO}_{2\text{ss}}$	Nonequilibrium.
		<sup>c</sup> 1000	60	$\text{IrO}_{2\text{ss}} + \text{TiO}_{2\text{ss}}$	
		<sup>c</sup> 1030	504	$\text{IrO}_{2\text{ss}} + \text{TiO}_{2\text{ss}}$	
		1035	2	$\text{IrO}_{2\text{ss}} + \text{TiO}_{2\text{ss}}$	Nonequilibrium.
		1040	2	$\text{IrO}_{2\text{ss}} + \text{TiO}_{2\text{ss}} + \text{Ir}$	
		1300	0.5	$\text{Ir} + \text{TiO}_{2\text{ss}} + \text{IrO}_2$	
15	85	<sup>d</sup> 1700	3	$\text{Ir} + \text{TiO}_2 + \text{IrO}_2$	Nonequilibrium; $\text{IrO}_2$ probably formed on cooling.
		900	20	$\text{IrO}_{2\text{ss}} + \text{TiO}_{2\text{ss}}$	
		<sup>c</sup> 1000	18	$\text{IrO}_{2\text{ss}} + \text{TiO}_{2\text{ss}}$	
		1030	1.5	$\text{IrO}_{2\text{ss}} + \text{TiO}_{2\text{ss}}$	Nonequilibrium.
		1035	2	$\text{IrO}_{2\text{ss}} + \text{TiO}_{2\text{ss}}$	
		1040	2	$\text{IrO}_{2\text{ss}} + \text{TiO}_{2\text{ss}} + \text{Ir}$	
		900	48	$\text{IrO}_{2\text{ss}} + \text{TiO}_{2\text{ss}}$	Quenched in ice water. Furnace cooled.
		<sup>c</sup> 1000	60	$\text{IrO}_{2\text{ss}} + \text{TiO}_{2\text{ss}}$	
		<sup>c</sup> 1000	336	$\text{IrO}_{2\text{ss}} + \text{TiO}_{2\text{ss}}$	
		1025	2	$\text{IrO}_{2\text{ss}} + \text{Ir}$	Nonequilibrium.
5	95	1030	2	$\text{IrO}_{2\text{ss}} + \text{Ir}$	
		1065	3	$\text{IrO}_{2\text{ss}} + \text{Ir} + \text{TiO}_{2\text{ss}}$	
		900	48	$\text{IrO}_{2\text{ss}} + \text{TiO}_{2\text{ss}}$	Very small amount of $\text{TiO}_{2\text{ss}}$ . Quenched in ice water. Furnace cooled.
		<sup>c</sup> 1000	60	$\text{IrO}_{2\text{ss}}$	
		<sup>c</sup> 1000	336	$\text{IrO}_{2\text{ss}}$	
		1020	2	$\text{IrO}_{2\text{ss}}$	Nonequilibrium.
		1025	2	$\text{IrO}_{2\text{ss}} + \text{Ir}$	
		1030	2	$\text{IrO}_{2\text{ss}} + \text{Ir}$	
		<sup>c</sup> 1030	504	$\text{IrO}_{2\text{ss}} + \text{Ir}$	Nonequilibrium. Nonequilibrium.
		900	45	$\text{IrO}_{2\text{ss}}$	
2	98	<sup>c</sup> 1000	18	$\text{IrO}_{2\text{ss}}$	
		1025	2	$\text{IrO}_{2\text{ss}} + \text{Ir}$	Nonequilibrium.
		1040	3	$\text{IrO}_{2\text{ss}} + \text{Ir}$	
		1050	2	$\text{IrO}_{2\text{ss}} + \text{Ir} + \text{TiO}_{2\text{ss}}$	
		1075	2.5	$\text{IrO}_{2\text{ss}} + \text{Ir} + \text{TiO}_{2\text{ss}}$	Nonequilibrium.
		1200	2	$\text{Ir} + \text{TiO}_{2\text{ss}}$	

<sup>a</sup> All specimens were heat treated at  $800^\circ\text{C}$  a minimum of 18 hr. Unless otherwise indicated, Vycor tubes (sealed at one end) were used for specimen containers and were air quenched.

<sup>b</sup> The phases identified are given in order of the relative amount present at room temperature.

<sup>c</sup> Sealed platinum tubes were used for specimen containers.

<sup>d</sup> Experiments were conducted in the iridium crucible induction furnace.

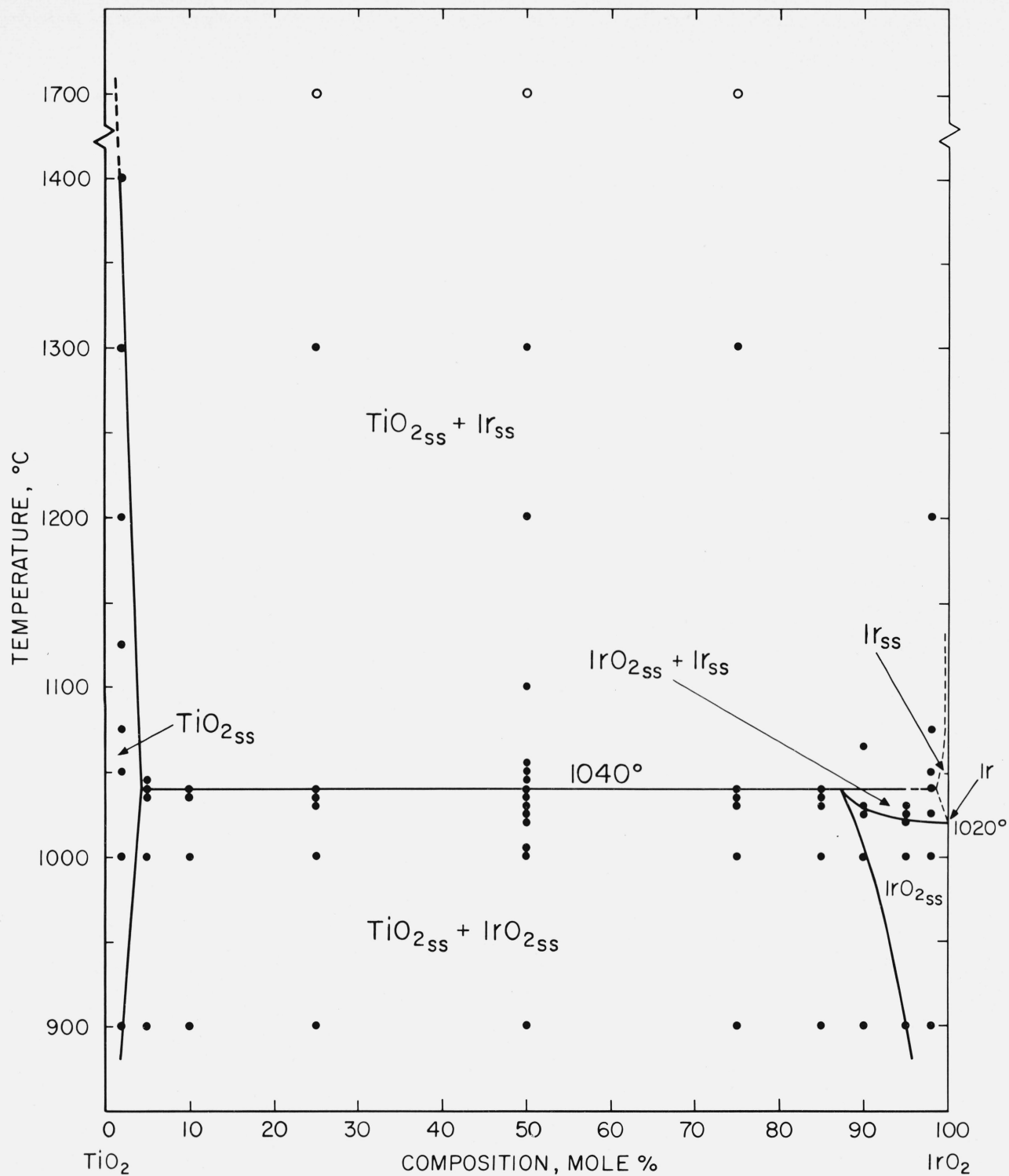


FIGURE 1. Phase equilibrium diagram for the  $\text{TiO}_2\text{-IrO}_2$  system in air.

● — compositions and temperatures of experiments conducted in quenching furnace.  
 ○ — compositions and temperatures of experiments conducted in the iridium crucible induction furnace.  
 ss — solid solution.

air at atmospheric pressure [7]. The dissociation is apparently a reversible process. Apparent metastable dissociation occurs when amorphous  $\text{IrO}_2$  is used. The data indicated a lowering of the dissociation temperature and was not consistent with the results from previous experiments. However, crystalline  $\text{IrO}_2$ , characterized by x-ray diffraction patterns after heating at 1000 °C for 18 hr, yielded dissociation data in good agreement with the earlier work [7, 8]. Metastable dissociation was also observed in the oxide- $\text{IrO}_2$  mixtures prior to the preliminary heat treatments.

No intermediate solid solution phases or binary compounds were detected in the  $\text{TiO}_2$ - $\text{IrO}_2$  system. Solid solution in  $\text{TiO}_2(\text{TiO}_{2\text{ss}})$  occurs with the addition of up to about 5 mole percent  $\text{IrO}_2$  at 1040 °C. At 1400 °C the extent of  $\text{TiO}_{2\text{ss}}$  decreased to less than 2 mole percent  $\text{IrO}_2$ , and at 1700 °C it was not detectable. Presumably at temperatures higher than 1400 °C, although not detected,  $\text{TiO}_{2\text{ss}}$  exists in decreasing amounts to the melting point of  $\text{TiO}_2$ . Melting was not observed in any of the experiments.

Up to 12 percent  $\text{TiO}_2$  in solid solution with  $\text{IrO}_2$  ( $\text{IrO}_{2\text{ss}}$ ) was found at the maximum dissociation temperature, 1040 °C. Figure 1 indicates  $\text{IrO}_{2\text{ss}}$  dissociates to two solid phases, Ir solid solution ( $\text{Ir}_{\text{ss}}$ ) and  $\text{TiO}_{2\text{ss}}$ . The  $\text{Ir}_{\text{ss}}$  apparently extends over such a small compositional range, it was not detected in this study. The  $\text{TiO}_{2\text{ss}}$  and  $\text{IrO}_{2\text{ss}}$  phases were identified by a shift in the x-ray reflections indicating a change in the unit cell dimensions.

At temperatures above 1040 °C, it could not be determined whether the system under consideration is a pseudo or a true binary system. The uncertainty is due to the inability to identify the type of  $\text{TiO}_{2\text{ss}}$  that exists above the dissociation temperature. No definite conclusion can be made in this study concerning the presence of  $\text{IrO}_2$  or Ir in the  $\text{TiO}_{2\text{ss}}$  phase. The  $\text{TiO}_{2\text{ss}}$  may be an oxygen deficient phase at the higher temperatures.

The equilibrium phase diagram for the  $\text{SnO}_2$ - $\text{IrO}_2$  system in air is given in figure 2. The pertinent data are listed in table 2. The diagram is similar to the  $\text{TiO}_2$ - $\text{IrO}_2$  system in many respects. No intermediate binary phases were detected. Only limited solid solubility in  $\text{IrO}_2$  was found to exist, extending to about 3 mole percent  $\text{SnO}_2$  at 1025 °C, where dissociation occurs. Solid solutions in either  $\text{SnO}_2$  or Ir were not detected.

Inasmuch as both  $\text{TiO}_2$  and  $\text{IrO}_2$  have the tetragonal, rutile type structure with similar unit cell dimensions and the same cationic radii (0.68 Å) [10], it was expected that larger regions of solid solubility than observed would exist. Several experiments were conducted in order to establish whether or not the results found in this study were indeed indicative of equilibrium conditions. Every effort was made through thorough mixing and various heating techniques to react the oxides. The data did not differ for long heats (3 weeks) versus short heats (few hours) and for quenched specimens versus furnace cooled specimens. The results were identical for experiments using sealed and unsealed tubes below the dissociation

TABLE 2. Experimental data for compositions in the  $\text{SnO}_2$ - $\text{IrO}_2$  system

Composition		Heat treatment <sup>a</sup>		X-ray diffraction analyses <sup>b</sup>	Remarks
$\text{SnO}_2$	$\text{IrO}_2$	Temp.	Time		
Mole %	Mole %	°C	hr		
95	5	900	18	$\text{SnO}_2 + \text{IrO}_{2\text{ss}}$	Very small amount of $\text{IrO}_2$ .
		1000	18	$\text{SnO}_2 + \text{IrO}_{2\text{ss}}$	
		<sup>c</sup> 1000	168	$\text{SnO}_2 + \text{IrO}_{2\text{ss}}$	
		1020	2.5	$\text{SnO}_2 + \text{IrO}_{2\text{ss}}$	Nonequilibrium. Nonequilibrium.
		1025	2	$\text{SnO}_2 + \text{IrO}_{2\text{ss}} + \text{Ir}$	
		1030	2.5	$\text{SnO}_2 + \text{IrO}_{2\text{ss}} + \text{Ir}$	
		1200	2.5	$\text{SnO}_2 + \text{Ir}$	
		1400	3	$\text{SnO}_2 + \text{Ir}$	
		900	20	$\text{SnO}_2 + \text{IrO}_{2\text{ss}}$	
		<sup>c</sup> 1000	168	$\text{SnO}_2 + \text{IrO}_{2\text{ss}}$	
90	10	1020	2.5	$\text{SnO}_2 + \text{IrO}_{2\text{ss}}$	Nonequilibrium. Nonequilibrium.
		1025	2	$\text{SnO}_2 + \text{IrO}_{2\text{ss}} + \text{Ir}$	
		1030	2	$\text{SnO}_2 + \text{IrO}_{2\text{ss}} + \text{Ir}$	
		1040	2	$\text{SnO}_2 + \text{IrO}_{2\text{ss}} + \text{Ir}$	
		75	25	$\text{SnO}_2 + \text{IrO}_{2\text{ss}}$	Quenched in ice water. Furnace cooled.
50	50	900	20	$\text{SnO}_2 + \text{IrO}_{2\text{ss}}$	
		<sup>c</sup> 1000	5.5	$\text{SnO}_2 + \text{IrO}_{2\text{ss}}$	
		<sup>c</sup> 1000	70	$\text{SnO}_2 + \text{IrO}_{2\text{ss}}$	
		1020	2	$\text{SnO}_2 + \text{IrO}_{2\text{ss}}$	
		1025	2	$\text{SnO}_2 + \text{IrO}_{2\text{ss}} + \text{Ir}$	
		900	20	$\text{SnO}_2 + \text{IrO}_{2\text{ss}}$	Nonequilibrium. Nonequilibrium. Nonequilibrium. Nonequilibrium. Nonequilibrium.
		<sup>c</sup> 1000	66	$\text{SnO}_2 + \text{IrO}_{2\text{ss}}$	
		<sup>c</sup> 1000	25	$\text{SnO}_2 + \text{IrO}_{2\text{ss}}$	
		1020	2	$\text{SnO}_2 + \text{IrO}_{2\text{ss}}$	
		1025	2	$\text{SnO}_2 + \text{IrO}_{2\text{ss}} + \text{Ir}$	
		1030	2	$\text{SnO}_2 + \text{IrO}_{2\text{ss}} + \text{Ir}$	
		1035	2	$\text{SnO}_2 + \text{IrO}_{2\text{ss}} + \text{Ir}$	
		1040	2	$\text{SnO}_2 + \text{IrO}_{2\text{ss}} + \text{Ir}$	
		1050	2	$\text{SnO}_2 + \text{IrO}_{2\text{ss}} + \text{Ir}$	
		1060	20	$\text{SnO}_2 + \text{Ir}$	
25	75	900	18	$\text{IrO}_{2\text{ss}} + \text{SnO}_2$	Nonequilibrium. Nonequilibrium.
		<sup>c</sup> 1000	168	$\text{IrO}_{2\text{ss}} + \text{SnO}_2$	
		1015	2	$\text{IrO}_{2\text{ss}} + \text{SnO}_2$	
		1020	2.5	$\text{IrO}_{2\text{ss}} + \text{SnO}_2$	
		1025	2	$\text{IrO}_{2\text{ss}} + \text{SnO}_2 + \text{Ir}$	
		900	20	$\text{IrO}_{2\text{ss}} + \text{SnO}_2$	
		<sup>c</sup> 1000	168	$\text{IrO}_{2\text{ss}} + \text{SnO}_2$	
		1015	3	$\text{IrO}_{2\text{ss}} + \text{SnO}_2$	
		1020	2	$\text{IrO}_{2\text{ss}} + \text{SnO}_2$	
		1025	2	$\text{IrO}_{2\text{ss}} + \text{SnO}_2 + \text{Ir}$	
10	90	1030	2.5	$\text{IrO}_{2\text{ss}} + \text{SnO}_2 + \text{Ir}$	Nonequilibrium. Nonequilibrium.
		900	18	$\text{IrO}_{2\text{ss}} + \text{SnO}_2$	
		<sup>c</sup> 1000	168	$\text{IrO}_{2\text{ss}} + \text{SnO}_2$	
		1015	3	$\text{IrO}_{2\text{ss}} + \text{SnO}_2$	
		1020	2	$\text{IrO}_{2\text{ss}} + \text{SnO}_2$	
		1025	2	$\text{IrO}_{2\text{ss}} + \text{SnO}_2 + \text{Ir}$	
		1030	2.5	$\text{IrO}_{2\text{ss}} + \text{SnO}_2 + \text{Ir}$	
		900	18	$\text{IrO}_{2\text{ss}} + \text{SnO}_2$	
		<sup>c</sup> 1000	168	$\text{IrO}_{2\text{ss}} + \text{SnO}_2$	
		1015	2	$\text{IrO}_{2\text{ss}} + \text{SnO}_2$	
5	95	1020	2	$\text{IrO}_{2\text{ss}} + \text{SnO}_2$	Nonequilibrium. Nonequilibrium.
		1025	2	$\text{IrO}_{2\text{ss}} + \text{SnO}_2 + \text{Ir}$	
		900	18	$\text{IrO}_{2\text{ss}} + \text{SnO}_2$	
		<sup>c</sup> 1000	168	$\text{IrO}_{2\text{ss}} + \text{SnO}_2$	
		1015	2	$\text{IrO}_{2\text{ss}} + \text{SnO}_2$	
		1020	2	$\text{IrO}_{2\text{ss}} + \text{SnO}_2$	
		1025	2	$\text{IrO}_{2\text{ss}} + \text{SnO}_2 + \text{Ir}$	
		900	18	$\text{IrO}_{2\text{ss}} + \text{SnO}_2$	
		<sup>c</sup> 1000	168	$\text{IrO}_{2\text{ss}} + \text{SnO}_2$	
		1015	2	$\text{IrO}_{2\text{ss}} + \text{SnO}_2$	
2.5	97.5	1020	2	$\text{IrO}_{2\text{ss}} + \text{SnO}_2$	Nonequilibrium. Nonequilibrium. Nonequilibrium.
		1025	2	$\text{IrO}_{2\text{ss}} + \text{SnO}_2 + \text{Ir}$	
		900	18	$\text{IrO}_{2\text{ss}} + \text{SnO}_2$	
		<sup>c</sup> 1000	168	$\text{IrO}_{2\text{ss}} + \text{SnO}_2$	
		1015	2	$\text{IrO}_{2\text{ss}} + \text{SnO}_2$	
		1020	2	$\text{IrO}_{2\text{ss}} + \text{SnO}_2$	
		1025	2	$\text{IrO}_{2\text{ss}} + \text{SnO}_2 + \text{Ir}$	
		1030	2	$\text{IrO}_{2\text{ss}} + \text{SnO}_2 + \text{Ir}$	
		900	18	$\text{IrO}_{2\text{ss}} + \text{SnO}_2$	
		<sup>c</sup> 1000	168	$\text{IrO}_{2\text{ss}} + \text{SnO}_2$	
1	99	1015	2	$\text{IrO}_{2\text{ss}}$	Very small amount of $\text{SnO}_2$ . Very small amount of $\text{SnO}_2$ .
		1020	2	$\text{IrO}_{2\text{ss}}$	
		1025	2	$\text{IrO}_{2\text{ss}}$	
		1035	2	$\text{IrO}_{2\text{ss}} + \text{Ir}$	
		1050	3	$\text{Ir} + \text{SnO}_2$	
		1060	4	$\text{Ir} + \text{SnO}_2$	
		900	18	$\text{IrO}_{2\text{ss}}$	
		<sup>c</sup> 1000	168	$\text{IrO}_{2\text{ss}}$	
		1015	2	$\text{IrO}_{2\text{ss}}$	
		1020	2	$\text{IrO}_{2\text{ss}}$	

<sup>a</sup> All specimens were heat treated at 800 °C a minimum of 18 hr. Unless otherwise indicated, Vycor tubes (sealed at one end) were used for specimen containers and were air quenched.

<sup>b</sup> The phases identified are given in order of the relative amount present at room temperature.

<sup>c</sup> Sealed platinum tubes were used for specimen containers.

tion temperatures. Hydrothermal experiments did not indicate any increase in oxide reaction.

It was thought that an unmixing dome might exist such as reported for the  $\text{TiO}_2$ - $\text{SnO}_2$  system [11]. High temperature x-ray diffraction data indicated that there was no unmixing on cooling in the  $\text{TiO}_2$ - $\text{IrO}_2$  system. The data indicate that the tendency for dissociation is so great that only limited solubility occurs. At higher temperatures and higher oxygen pressures a miscibility range may exist.

Iridium metal seems quite acceptable as a container material for a study of  $\text{SnO}_2$  in air above 1025 °C. The oxidation of Ir at low temperatures does not appreciably detract from its use as a container at high tem-

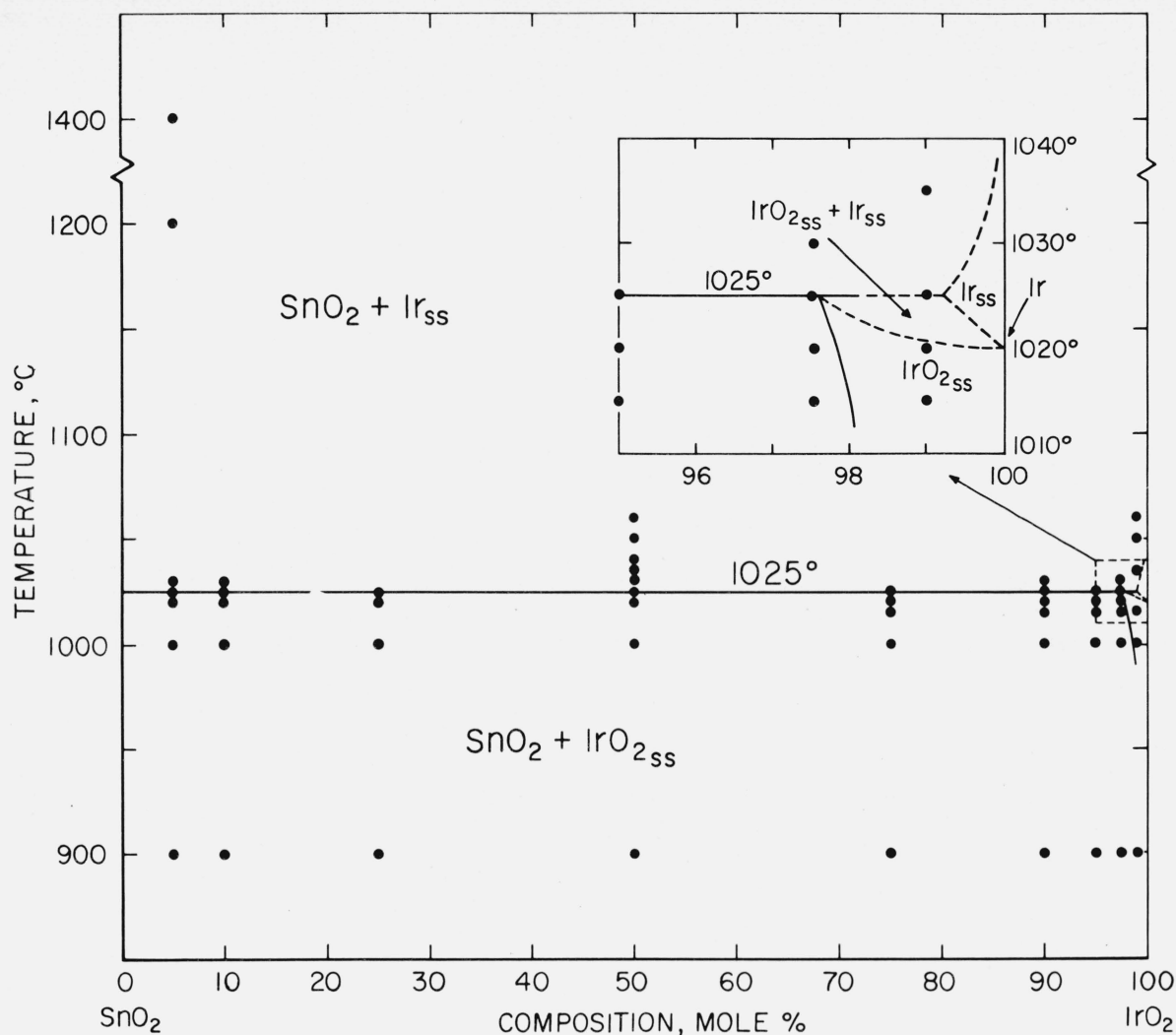


FIGURE 2. Phase equilibrium diagram for the  $\text{SnO}_2\text{-IrO}_2$  system in air.  
 Insert shows expanded view of diagram from 95 to 100 mole percent  $\text{IrO}_2$  and from 1010 to 1040 °C.  
 •—compositions and temperatures of experiments conducted in quenching furnace.  
 ss—solid solution.

peratures. The fact that  $\text{TiO}_{2\text{ss}}$  was not detected above 1400 °C, does not eliminate possible problems in the use of Ir as a container material for a study of  $\text{TiO}_2$  in air.

#### 4.2. Summary

Equilibrium phase diagrams for the  $\text{TiO}_2\text{-IrO}_2$  and  $\text{SnO}_2\text{-IrO}_2$  systems were determined in air. Selected mixtures in the systems were studied by x-ray diffraction after various heat treatments. In the  $\text{TiO}_2\text{-IrO}_2$  system, solid solution in  $\text{TiO}_2$  occurs up to about 5 mole percent  $\text{IrO}_2$  at 1040 °C. Solid solution in  $\text{IrO}_2$  occurs up to about 12 mole percent  $\text{TiO}_2$  at the maximum dissociation temperature of 1040 °C.

The  $\text{SnO}_2\text{-IrO}_2$  system is similar to  $\text{TiO}_2\text{-IrO}_2$  system in many respects. Limited solid solubility of  $\text{IrO}_2$  was found with the addition of about 3 mole percent  $\text{SnO}_2$  at 1025 °C, the temperature at which dissociation occurs.

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